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Reactions of polycyclic ketones with Dimethoxycarbene; a convenient route for a one-pot preparation of some alpha-hydroxycarboxylic acid esters

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Abstract: Polycyclic 'cage' ketones, such as pentacyclo[5.4.0.02,6.03,10.05,9]undecan-8-one (10), pentacyclo[5.4.0.02,6.03,1
8,11-dione (11), and adamantan-2-one (16) were treated with the nucleophilic dimethoxycarbene (DMC; 1), which was generated thermally from 2,5-dihydro-2,2-dimethoxy-5,5-dimethyl-1,3,4-oxadiazole (4a) in boiling toluene. In this 'one-pot' procedure, the ahydroxycarboxylic acid ester 12 or a corresponding derivative 15 or 17 was obtained (Schemes 4 – 7). Additionally, 'cage' thione 21 was treated with DMC under the same conditions yielding dimethoxythiirane 22 (Scheme 8). Subsequent hydrolysis or desulfurization (followed by hydrolysis on silica gel) of 22 gave alpha-mercaptocarboxylate 25 and the corresponding desulfurized ester 24, respectively. In all cases, the addition of DMC occurred stereoselectively, and the addition from the exo-face is postulated to explain the structures of the isolated products.

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Reactions of Polycyclic Ketones with Dimethoxycarbene; a Convenient Route for a 'One-pot' Preparation of Some α-Hydroxycarboxylic Esters

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Polycyclic 'cage' ketones, such as pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8-one (**10**), pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (**11**), and adamantanone (**16**) were reacted with the nucleophilic dimethoxycarbene (**1**, DMC), which was generated thermally from 2,5-dihydro-2,2-dimethoxy-5,5-dimethyl-l,3,4-oxadiazole (**4a**) in boiling toluene. In this 'one-pot' procedure, the α-hydroxycarboxylic esters **12**, **15**, and **17** were obtained. Additionally, 'cage' thione **21** was reacted with DMC under the same conditions yielding dimethoxythiirane **22**. Subsequent hydrolysis or desulfurization (followed by hydrolysis on silicagel) of **22** gave α-mercaptocarboxylic ester **25** and the corresponding desulfurized ester **24**, respectively. In all cases, the addition of DMC occurs stereoselectively, and the addition from the *exo*-face is postulated to explain the structures of the isolated products.

1. Introduction. - Widely known classical carbenes are electrophilic, reactive intermediates, and methylene, conveniently generated from diazomethane, is the simplest example. The replacement of H-atoms in the methylene molecule by heteroatoms such as O, N or S leads to a carbene with an inverted character, *i.e.*, a nucleophilic one. Among numerous examples of heteroatom-substituted carbenes [1], dimethoxycarbene (**1**, DMC) is a simple one, which is relatively easy to generate (*Scheme 1*). In the early 1970´s, *Hoffmann* and coworkers generated DMC for the first time by heating the precursor **2** to 140°. In this process, tetrachlorobiphenyl was found as a side product [2]. In 1987, *Moss* and coworkers reported on the synthesis of dimethoxydiazirine (**3**), which subsequently was used as a DMC source *via* thermal or photochemical decomposition. In this case, N_2 is the only side product [3]. This method is very clean, but diazirine **3** is a highly explosive compound and therefore difficult to handle.

Scheme 1

A few years ago, *Warkentin* and coworkers prepared 2,5-dihydro-2,2-dimethoxy-5,5-dimethyl-l,3,4-oxadiazole (**4a**) and used it as a quite stable precursor, which, during heating, smoothly generates DMC accompanied by acetone and N_2 as side products [4a]. Recently, a new 1,3,4-oxadiazole derivative **4b** was described, and in this case DMC is generated already at 50° [4b]. Using matrix isolation and computational methods, the spectroscopic properties of DMC, which was generated thermally in the gas phase from **4a**, were established and conformational studies described [5a]. Using the same methodology, the dithioalkoxycarbene (*Seebach*'s carbene) was generated and trapped at low temperature, and subsequently characterized by means of spectroscopic methods [5b].

Several reactions of DMC with C,C- [6][7] and C,X-multiple bonds [8-11] are known. The results of the reactions of DMC with dimethyl actetylenedicarboxylate (DMAD) in the presence of aldehydes, diphenylketene, arylisocyanates, as well as ketones, showed the possible applications of this carbene in synthesis. Particularly, the formation of the furan ring in compounds of type **5** illustrates a stepwise process, in which DMC attacks the triple bond of DMAD, and the zwitterionic intermediate is trapped subsequently by the aldehyde [12] (*Scheme 2*). Similarly, DMC reacts with two molecules of arylisocyanate to give hydantoine derivatives **6** [13]. In the case of the reaction of DMC with maleic anhydride, an insertion process is observed which yields the pyran derivative **7** [14]. Recently, *Warkentin´*s group has found that simple, non-congested ketones like cyclohexanone react with DMC to form *spiro*-dimethoxyoxiranes of type **8**, whereas cyclobutanone reacts to give the ring-enlarged product **9** [8].

Scheme 2

In recent decades, polycyclic compounds attracted considerable attention by several investigators worldwide [15], and reactions of their carbonyl derivatives with nucleophilic agents have extensively been explored [16-18]. However, to the best of our knowledge, the 'cage' ketones have not yet been explored in the reactions with DMC. In the present work, we describe the results obtained in reactions of thermally generated **1** (from **4a**) with carbonyl and thiocarbonyl 'cage' compounds derived from ketone **10**.

2. Results and Discussion. - *Warkentin* reported the reactions of DMC with simple cyclic ketones and diketones, showing the formation of products of either addition to the C=O bond

or insertion into C–C bonds, *e.g.*, compounds **8** and **9**, respectively [8] (*Scheme 2*). Keeping in mind these results, the reactions of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8-one (**10**) and pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (**11**) with DMC have been studied. In analogy to previously described results [8], we expected the formation of either a 'cage' substituted oxirane or a masked 1,2-dione, exemplified for ketone **10** in *Scheme 3*. It is worth of mentioning that *Warkentin* carried out the analogous reactions in sealed tubes and dry and degassed benzene. In our experiments, commercial toluene was used and the mixtures were heated under reflux without application of an inert gas atmosphere.

Scheme 3

In the first attempt, the reaction of the 'cage' monoketone **10** was carried out with an equimolar amount of the DMC precursor **4a**, but the conversion was very low. However, heating of **10** with a 2.5-fold excess of **4a** led to satisfactory results. After chromatographic workup and additional recrystallization, a colorless solid was obtained. Surprisingly, the ^{1}H-NMR spectrum showed only one signal for a MeO group at 3.71 ppm. The IR spectrum exhibited the presence of a strong C=O band at 1711 cm^{-1} and a broad absorption at 3400 cm^{-1} for the OH-group. Based on these data, the structure of the ester **12** (*Scheme 4*) was proposed for the isolated product. This structure was unambiguously confirmed by a crystal structure analysis (*Figure*).

Scheme 4

Figure. *ORTEP Plot* [19] *of the molecular structure of* **12** (50% probability ellipsoids, arbitrary numbering of atoms)

The postulated reaction mechanism is presented in *Scheme 4*. Initially, the nucleophilic DMC attacks the carbonyl group to give the thermolabile oxirane **13** or the zwitterion **14**, which probably exist in equilibrium. The latter is effectively trapped by traces of H_2O present in the solvent, and subsequent elimination of MeOH leads to **12**.

The reaction of the dione **11** was carried out under the same conditions, and after *ca*. 8 h, the starting material has been consumed completely. After chromatographic workup, a colorless solid was obtained, and the analysis of the ^{1}H-NMR spectrum showed the presence of only one signal for MeO at 3.80 ppm. Unexpectedly, six signals were found in the ^{13}C-NMR spectrum, suggesting a symmetric structure of the cage moiety of the product. The CI-MS revealed the base peak at m/z = 294 $[M+NH_4]^+$. Based on this data, the structure of the oxa-bridged diester **15** was assigned to the isolated compound. Probably, in this reaction, both carbonyl groups react with **1** and subsequently, the initially formed bis(hydroxycarboxylic ester) undergoes dehydration to give **15** as the final product (*Scheme 5*). The corresponding bis(hydroxycarboxylic acid) has been obtained earlier in a multistep synthesis by *Marchand* and co-workers [20], and the reported spectroscopic data are comparable with those of **15**. In particular, the ^{13}C-NMR signal of C(3) and C(5) of the acid located at 94.4 ppm fits very well with the corresponding signal of **15** at 94.9 ppm.

Scheme 5

Adamantanone (**16**), one of the best-known 'cage' ketones, has not yet been examined in the reaction with DMC and it was obvious to include it in our study. In this case, after 6 h in refluxing toluene using excess **4a**, the α-hydroxycarboxylic ester **17** was obtained in good yield. This product has already been described, but its synthesis from **16** is a tedious four-step process, which includes reactions with toxic reagents such as diazomethane and selenium dioxide [21] (*Scheme 6*). Therefore, the reaction with DMC represents a very much improved synthesis.

Scheme 6

Recently, the reaction of adamantanethione (**18**) with DMC was reported, in which thiirane **19** was obtained in excellent yield. Subsequent hydrolysis of **19** led to α-mercaptoester **20** [9] (*Scheme 7*).

Scheme 7

Now, we reacted the 'cage' thione **21** with an equimolar amount of **4a**, and after 2 h, the red color of **21** vanished. Chromatographic workup gave thiirane **22** as a colorless oil (*Scheme 8*). In the ^{13}C-NMR spectrum, the characteristic signals for C(3) and C(2) of the thiirane ring located at 58.2 ppm and 105.9 ppm, respectively, were comparable with the data collected for the adamantane derivative **19** [9]. Moreover, the ^{1}H-NMR spectrum showed two signals at 3.35 and 3.53 ppm for two MeO groups, which confirmed the formation of only one stereoisomer with the S-atom probably located at the *endo*-position. This supposition is

supported by the X-ray crystal structure determination of the structures of some [2+3]-cycloadducts obtained from **21** [17].

Subsequently, thiirane **22** was desulfurized to yield dimethyl ketene acetal **23**, which can be considered as the masked form of the corresponding ketene. First attempts of desufurization were carried out with frequently used Ph_3P, but in this case, after several hours of heating, only unchanged **22** was recovered. However, when Ph_3P was replaced by freshly prepared *Raney*-Ni, the reaction in boiling EtOH was complete after 8 h (monitored by TLC). After chromatographic workup, instead of the desired compound **23**, the ester **24** was obtained as the only product. It is likely that the initially formed reactive derivative **23** reacts with traces of water to form **24**. Interestingly, in the ^{1}H-NMR spectrum, only one signal for a MeO group at 3.68 ppm was detected, and this result confirms again that the reaction occurred stereoselectively.

Scheme 8

On the other hand, the hydrolysis of thiirane **22** was carried out at room temperature in acetone solution containing a mixture of trifluoroacetic acid (TFA) and H_2O. After 48 h, the reaction was complete (TLC monitoring). In the IR spectrum of the chromatographically isolated product, the absorption band at 2560 cm^{-1} was assigned to the SH group, and the ^{1}H-NMR spectrum showed a singlet for MeO located at 3.62 ppm that again proved the presence of only one stereoisomer. These data allowed the identification of the product of the hydrolysis as the expected α-mercaptocarboxylic ester **25** (*Scheme 8*).

In summary, the reactions of thermally generated dimethoxycarbene (DMC, **1**) with polycyclic 'cage' ketones **10**, **11** and **16** as well as thioketone **21** were carried out successfully. The observed reactivity of thioketone **21** and 'cage' monoketone **10** towards **1** showed that the C=S group reacts faster than the corresponding C=O group. In contrast to *Warkentin*'s report [8], the formation of an oxirane or insertion products has not been observed using the 'cage' ketones under the chosen reaction conditions. Instead, esters **12**, **15**, and **17** were isolated as final products. In all cases, the addition of DMC occurred stereoselectively from the *exo*-face, which results in the formation of products containing the ester group in the *exo*-position. In the case of thione **21**, the addition of DMC yields the thiirane **22**, in which the S-atom is *endo*-oriented. In general, the study showed that the reactions of 'cage'-ketones with DMC in commercial toluene under reflux lead to α-hydroxycarboxylic esters in a 'one-pot' procedure. This methodology offers an alternative and convenient approach to esters of this type, which are hitherto available only *via* multi-step procedures.

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Experimental Part

1. *General.* M.p. were determined in capillaries (*Melt-Temp. II, Aldrich*); uncorrected. IR spectra: *NEXUS FT-IR* spectrophotometer; in KBr. ^{1}H- and ^{13}C-NMR spectra: *Bruker AC 300* instrument (300 and 75.5 MHz, resp.), in $CDCl_3$, using TMS ($\delta = 0$ ppm) as an internal standard. The multiplicity of the ^{13}C signals was deduced from DEPT spectra. MS: *Finnigan MAT-90,* CI-mode (NH_3). HRMS: *Finnigan MAT SSQ 710*.

2. *Starting Materials. 2,5-Dihydro-2,2-dimethoxy-5,5-dimethyl-l,3,4-oxadiazole* (**4a**) [4a], *pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8-one* (**10**) [17], and *pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecan-8-thione* (**22**) [18] were prepared according to the known protocols. *Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8,11-dione* (**11**) and *adamantanone* (**16**) are commercially available.

3. *Reactions with DMC.* – 3.1. *Methyl 8-Hydroxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8-carboxylate* (**12**). Monoketone **10** (320 mg, 2 mmol) and **4a** (800 mg, 5 mmol) were dissolved in toluene (4 ml), and the mixture was heated to reflux for 8 h in an open-air apparatus. Then, toluene was removed under reduced pressure and the crude product obtained was purified chromatographically (SiO_2, hexane and increasing amounts of Et_2O) to yield **12** as a colorless solid (170 mg, 36%). M.p. 64–66° (petroleum ether). IR: 3408*s*, 2955*s*, 2865*m*, 1711*s*, 1261*m*, 1110*m*, 715*w*. ^{1}H-NMR: 1.05–1.10 (*m*, 1 H); 1.20, 1.66 (*AB*, J_{AB} = 10, 2 H); 2.17–2.30 (*m*, 3 H); 2.45–2.93 (*m*, 7 H); 3.71 (*s*, 3 H). ^{13}C-NMR: 28.9 (*t*), 34.8 (*t*), 36.0 (*d*), 40.0 (*d*), 41.5 (*d*), 41.7 (*d*), 43.2 (*d*), 43.4 (*d*), 46.8 (*d*), 48.9 (*d*), 52.0 (*q*), 82.5 (*s*), 176.0 (*s*, C=O). CI-MS: 238 $[M+NH_4]^+$. Anal. calc. for $C_{13}H_{16}O_3$ (220.27): C 70.89, H 7.32; found: C 71.84, H 7.69.

3.2. *Methyl 4-Oxahexacyclo[5.4.1.0.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane-3,5-dicarboxylate* (**15**). Dione **11** (348 mg, 2 mmol) and **4a** (800 mg, 5 mmol) were dissolved in toluene (4 ml), and the mixture was heated to reflux for 8 h in an open-air apparatus. Workup as described in *Section 3.1* (CC, SiO_2, CH_2Cl_2/MeOH, 98:2) yielded **15** as a colorless solid (105 mg, 19%). M.p. 140–142° (hexane/CH_2Cl_2). IR: 3432*m*, 2983*m*, 2957*m*, 2889*w*, 2867*w*, 1756*s*, 1284*s*, 1096*s*, 734*w*. ^{1}H-NMR: 1.64, 2.00 (*AB*, J_{AB} = 11, 2 H); 2.70–2.88 (*m*, 4 H); 2.98–3.10 (*m*, 4 H); 3.80 (*s*, 3 H). ^{13}C-NMR: 42.3 (*d*), 43.3 (*t*), 45.3 (*d*), 49.4 (*d*), 52.3 (*q*), 58.8 (*d*), 94.9 (*s*), 170.9 (*s*, C=O). CI-MS: 294 [*M*+NH_4]$^+$.

3.3. *Methyl 2-Hydroxyadamantane-2-carboxylate* (**17**). Adamantanone (**16**; 200 mg, 1.3 mmol) and **4a** (480 mg, 3 mmol) were dissolved in toluene (4 ml), and the mixture was heated to reflux for 6 h in an open-air apparatus. Then, toluene was removed under reduced pressure and the crude product was treated with petroleum ether yielding **17** as a colorless solid (108 mg, 51%). M.p. 87–88° (petroleum ether; [16b]: m.p. 88–89°). IR: 3430*s*, 2918*s*, 2857*m*, 1712*s*, 1264*s*, 1096*m*, 940*w*, 767*w*. ^{1}H-NMR: 1.55–1.62 (*m*, 2 H); 1.69 (*br. s*-like, 2 H); 1.79 (*br. s*-like, 6 H); 2.17–2.24 (*m*, 4 H); 2.26 (*s*, 1 H); 3.75 (*s*, 3 H). ^{13}C-NMR: 26.6 (*d*), 26.8 (*d*), 32.2 (*t*), 34.5 (*d*), 34.9 (*t*), 37.4 (*t*), 51.9 (*q*), 78.2 (*s*), 174.5 (*s*, C=O).

3.4. *2,2-Dimethoxyspiro[thiirane-2,8'-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane]* (**22**). Thione **21** (356 mg, 2 mmol) and **4a** (350 mg, 2.1 mmol) were dissolved in toluene (4 ml), and the mixture was heated to reflux for 2 h in an open-air apparatus. Workup as described in *Section 3.1* (CC, SiO_2, hexane with increasing amounts of CH_2Cl_2) yielded **22** as a colorless oil (105 mg, 60%). IR (film): 2958*s*, 2863*m*, 2833*m*, 1732*w*, 1452*m*, 1376*m*, 1104*s*, 1064*m*, 925*w*, 818*s*. ^{1}H-NMR: 1.15–1.21 (*m*, 1 H); 1.29, 1.72 (*AB*, J_{AB} = 10, 2 H); 2.08–2.85 (*m*, 9 H); 3.35 (*s*, 3 H); 3.53 (*s*, 3 H). ^{13}C-NMR: 27.2 (*t*), 34.5 (*t*), 35.9 (*d*), 39.6 (*d*), 42.4 (*d*), 42.8 (*d*), 43.1 (*d*), 44.2 (*d*), 46.6 (*d*), 46.9 (*d*), 55.0 (*q*), 55.6 (*q*), 58.3 (*s*), 105.9 (*s*). CI-MS: 251 [*M*+1]$^+$.

4. Desulfurization of thiirane **22***; Methyl Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8-carboxylate* (**24**). Thiirane **22** (80 mg, 0.3 mmol) was dissolved in EtOH (4 ml) and a suspension of freshly prepared *Raney*-Ni in EtOH (*ca*. 3 ml) was added at r.t. The mixture was heated to reflux for 8 h, and then *Raney*-Ni was removed by filtration. Chromatography of the residue (SiO_2 coated plates, 2 mm layer, petroleum ether/CH_2Cl_2, 3:2) yielded **24** as a colorless oil (32 mg, 45%). IR (film): 3440*w*, 2961*s*, 2866*s*, 1728*s*, 1254*s*, 1036*w*. ^{1}H-NMR: 1.05–1.10 (*m*, 1 H); 1.18–1.26 (*m*, 3 H); 1.69 (*d*-like, J = 10, 1 H); 2.20–2.48 (*m*, 4 H); 2.58–2.79 (*m*, 4 H); 2.90–2.96 (*m*, 1 H); 3.68 (*s*, 3 H). ^{13}C-NMR: 28.3 (*t*), 34.1 (*t*), 36.5 (*d*), 37.2 (*d*), 41.9 (*d*), 42.2 (*d*), 42.5 (*d*), 43.5 (*d*), 45.9 (*d*), 46.1 (*d*), 46.6 (*d*), 51.4 (*q*), 175.2 (*s*, C=O). HRMS: Calc. for $C_{13}H_{16}O_2$: 204.11503; found: 204.11434.

5. Hydrolysis of thiirane **22***; Methyl 8-Mercaptopentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8-carboxylate* (**25**). Thiirane **22** (80 mg, 0.3 mmol) was dissolved in acetone (4 ml), 3-4 drops of CF_3COOH/H_2O (1:1) were added, and the mixture was stirred at r.t. After 2 d, acetone was removed under reduced pressure, the residue was extracted with CH_2Cl_2, and the extract was washed with 10% $NaHCO_3$ and H_2O and was dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was purified chromatographically (SiO_2 plates, 2 mm layer, hexane/Et_2O, 1:1) yielding **25** as a colorless oil (60 mg, 66%). IR (film): 3440*w*, 2963*s*, 2866*s*, 2560*w* (SH), 1732*s*, 1228*s*, 914*w*. ^{1}H-NMR: 0.96–1.01 (*m*, 1 H); 1.13, 1.62 (*AB*, J_{AB} = 10, 2 H); 2.00–2.05 (*m*, 1 H); 2.10 (*s*, 1 H); 2.17–2.22 (*m*, 1 H); 2.40–2.65 (*m*, 5 H); 2.72–2.78 (*m*, 1 H); 2.91–2.95 (*m*, 1 H); 3.62 (*s*, 3 H). ^{13}C-NMR: 27.7 (*t*), 33.7 (*t*), 35.7 (*d*), 41.6 (*d*), 42.0 (*d*), 42.2 (*d*), 42.7 (*d*), 45.3 (*d*), 47.3 (*d*), 49.4 (*d*), 52.5 (*q*), 53.2 (*s*), 174.3 (*s*, C=O). HRMS: Calc. for $C_{13}H_{16}O_2S$: 236.08710; found: 236.08704.

6. *X-Ray Crystal-Structure Determination of* **12** (*Table* and *Fig. 1*)[1]). All measurements were performed on a *Nonius KappaCCD* diffractometer [22] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream* 700 cooler. The data collection and refinement parameters are given in the *Table*, and a view of the molecule is shown in the *Figure*. Data reduction was performed with *HKL Denzo* and *Scalepack* [23]. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Equivalent reflections were merged. The structure was solved by direct methods using SIR92 [24], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. The hydroxy H-atom was placed in the position indicated by a difference electron density map and its position was allowed to refine together with an isotropic displacement parameter. All remaining H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me group). The refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied. Two reflections, whose intensities were considered to be extreme outliers, were omitted from the final refinement. Neutral atom scattering factors for non-H-atoms were taken from [25a], and the scattering factors for H-atoms were taken from [26]. Anomalous dispersion effects were included in F_c [27]; the values for f' and f'' were those of

[1]) CCDC-634664 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre*, *via* www.ccdc.cam.ac.uk/data_request/cif.

[25b]. The values of the mass attenuation coefficients are those of [25c]. All calculations were performed using the *SHELXL97* [28] program.

Table. *Crystallographic Data for Compound* **12**

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Table. *Crystallographic Data for Compound* **12**

	12
Crystallized from	petroleum ether
Empirical formula	$C_{13}H_{16}O_3$
Formula weight	220.27
Crystal color, habit	colorless, prism
Crystal dimensions [mm]	0.10 × 0.15 × 0.22
Temperature [K]	160(1)
Crystal system	monoclinic
Space group	$P2_1/c$
Z	4
Reflections for cell determination	2562
2θ range for cell determination [°]	4–55
Unit cell parameters a [Å]	9.7802(4)
b [Å]	7.7082(3)
c [Å]	14.0749(4)
β [°]	100.911(2)
V [Å^3]	1041.89(7)
D_X [g cm^{-3}]	1.404
μ(MoK_α) [mm^{-1}]	0.0985
Scan type	ϕ and ω
2θ(max) [°]	55
Total reflections measured	22866
Symmetry independent reflections	2390
Reflections with $I > 2\sigma(I)$	1817
Reflections used in refinement	2388
Parameters refined	151
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0470
$wR(F^2)$ (all data)	0.1243
Weighting parameters [a; b][a])	0.0558; 0.3906
Goodness of fit	1.029
Secondary extinction coefficient	0.021(5)
Final Δ_{max}/σ	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.22; –0.22

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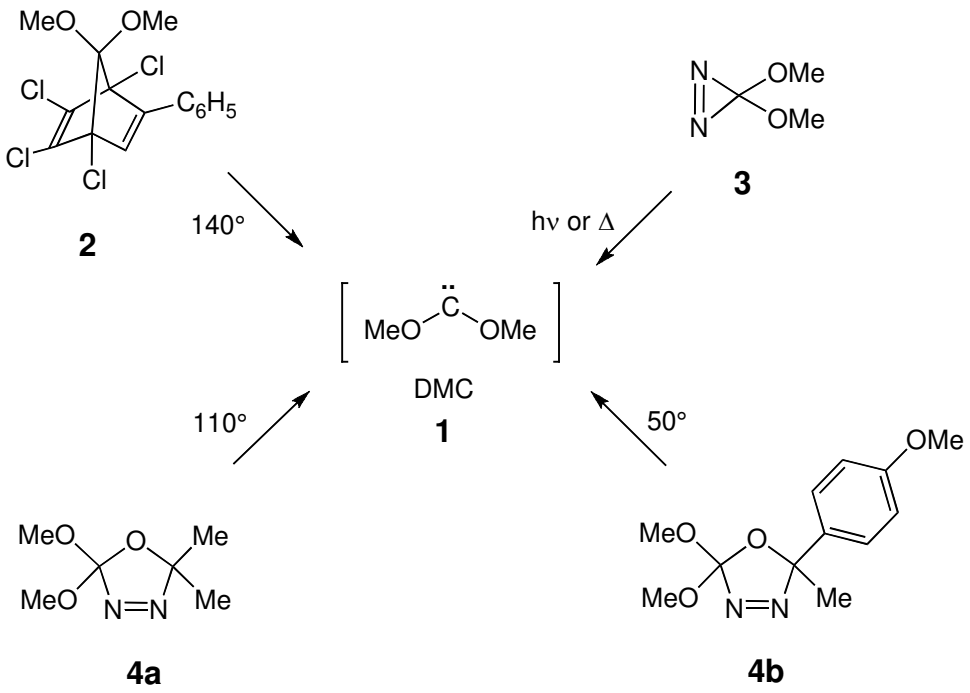
a) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$

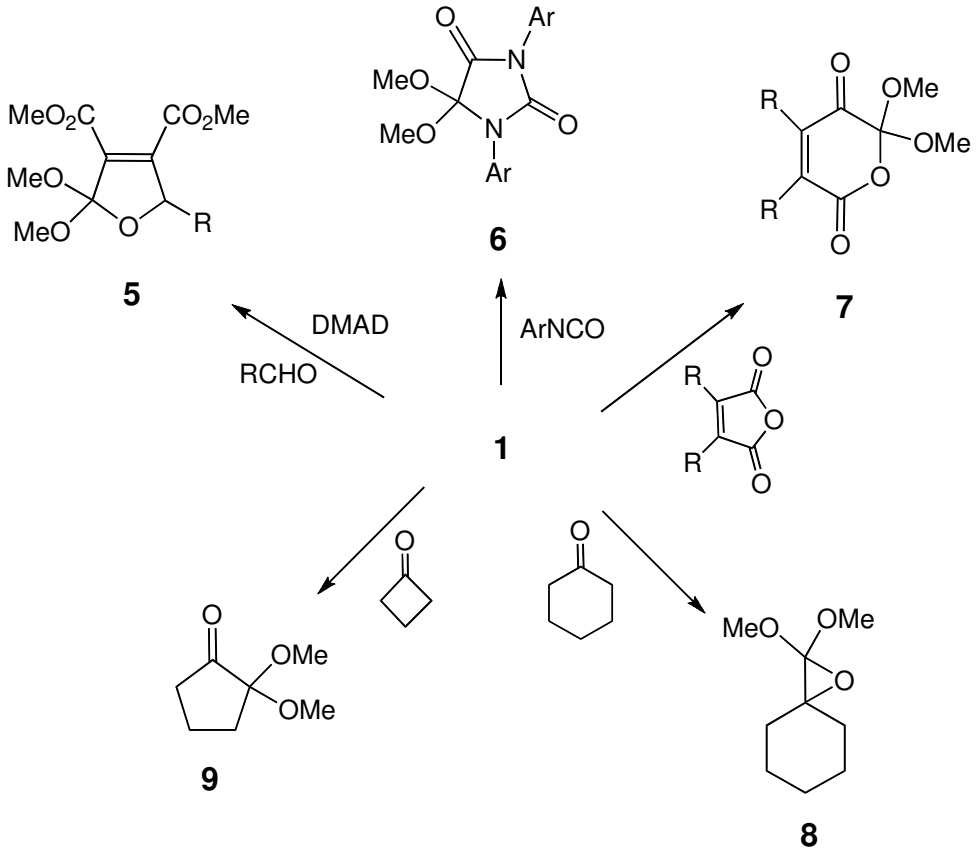
Legends

Figure. *ORTEP Plot* [19] *of the molecular structure of* **12** (50% probability ellipsoids, arbitrary numbering of the atoms)

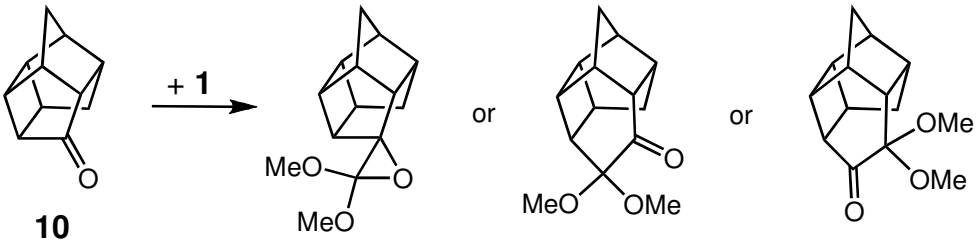
Scheme 1


MeO
OMe
Cl
Cl
C_6H_5
Cl
Cl
2
140°
N
N
OMe
OMe
3
hν or Δ
MeO
C
OMe
DMC
1
110°
50°
MeO
O
Me
MeO
N=N
Me
4a
OMe
MeO
O
MeO
N=N
Me
4b

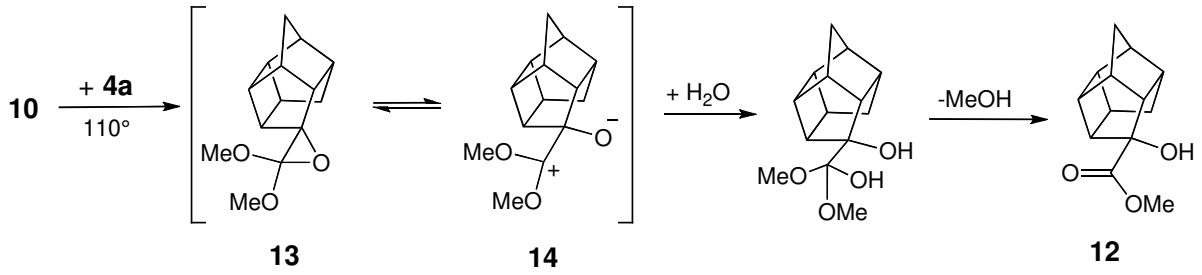
Scheme 2



Scheme 3

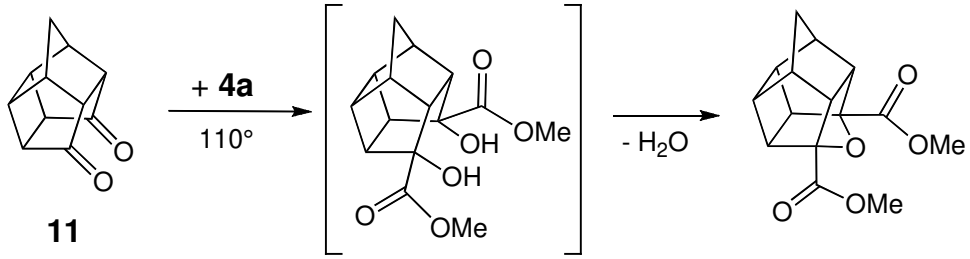


Scheme 4



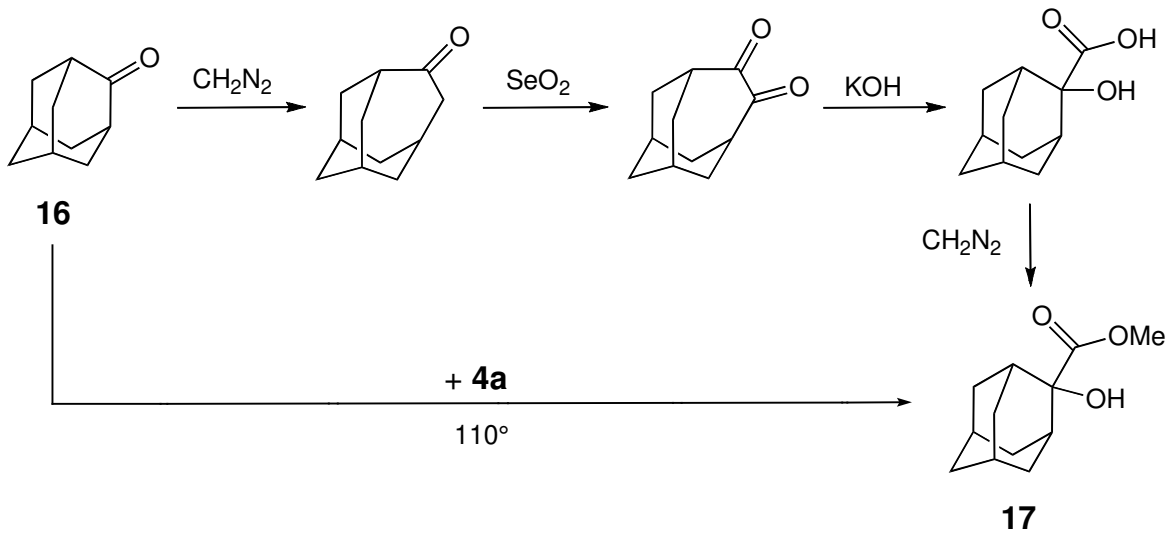
13 **14** **12**

Scheme 5

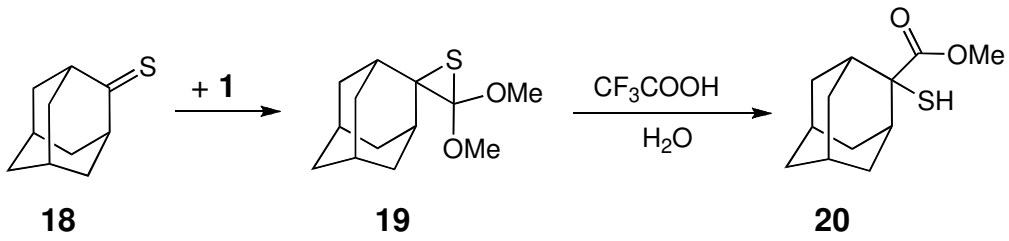


11 **15**

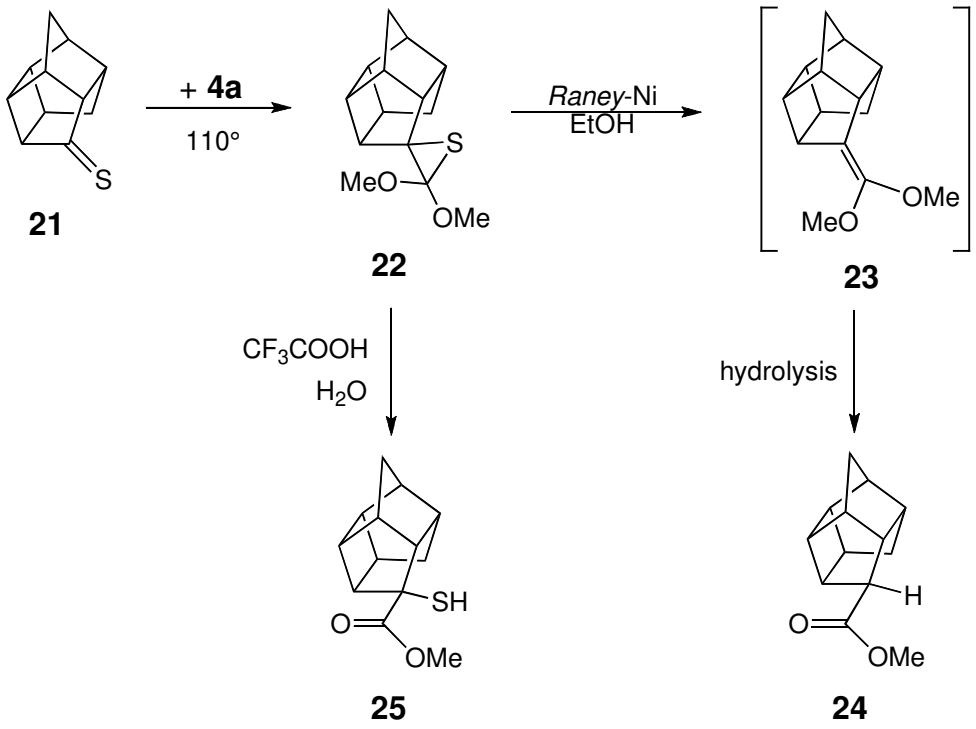
Scheme 6



Scheme 7



Scheme 8



Figure